

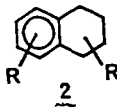
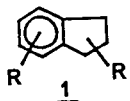
SYNTHESIS OF ALKYLATED INDANES AND TETRALINS
FOR USE IN FOSSIL FUEL ANALYSIS

By

D. S. Watt, M. Adamczyk, and D. A. Netzel
Department of Chemistry, University of Wyoming
and Department of Energy, Laramie Energy Technology Center
Laramie, Wyoming 82070

ABSTRACT

The availability of authentic hydrocarbon samples in the substituted indane and tetralin families would facilitate the analysis of certain fossil fuel mixtures. We have developed general procedures for the efficient preparation of simple alkylated indanes 1 tetralins 2 from common precursors. We have examined the ^{13}C NMR and mass spectral fragmentation data for hydrocarbons 1 and 2 in detail.



A TIME-TEMPERATURE-CONCENTRATION MATRIX FOR INDUCED
SEDIMENT FORMATION IN SHALE DIESEL FUEL

By

J. V. Cooney, E. J. Beal, and R. N. Hazlett
Naval Research Laboratory, Code 6180, Washington, D.C. 20375

INTRODUCTION

Deterioration in fuel quality with time has been a continuing problem in the utilization of middle distillate fuels. These stability problems will intensify as we develop alternative sources of fuel, such as shale oil and coal. Present knowledge has suggested that for some fuels, nitrogen heterocycles may play a causative role in the formation of insoluble sediments and gums under conditions of ambient and accelerated storage (1). In light of the high costs of fuel processing, substantial savings could be realized if it were possible to identify those nitrogen heterocycles which are most actively involved in the formation of insoluble material. Currently, it appears that relatively non-basic nitrogen heterocycles, particularly those which contain alkyl groups in certain positions, may be the most troublesome (2). However, in other fuels and under different test conditions, basic nitrogen compounds may play a significant role (3).

In addressing this subject, we are defining the stability of shale-derived diesel fuel marine (DFM), stressing the sample under accelerated storage conditions, and determining the amount of total insoluble material produced. This report describes results obtained when 2,5-dimethylpyrrole (DMP) was used as a dopant in a time-temperature-concentration matrix. Results of a survey of other nitrogen compounds as fuel additives are also presented.

EXPERIMENTAL

Storage Test Techniques

The experimental procedures used were developed from reported methods (2). In summary, 300 ml samples of filtered fuel were stressed in the dark in 500 ml screw-cap borosilicate Erlenmeyer flasks (Teflon-lined caps). All samples were run in duplicate. Vented tests were accomplished by using modified screw caps which were drilled to hold 6 mm glass tubing (with glass wool plugs). After stress, test flasks were allowed to cool to room temperature before being filtered under slight vacuum through a double layer of Gelman glass fiber filter paper. Flask contents were then rinsed with several ml of *n*-heptane, with additional sediment being collected on the filter paper. The filter cake was rinsed with *n*-heptane to remove adsorbed fuel. The flasks and filter holders were heated (120°C) under vacuum for twelve hours, allowed to equilibrate on a benchtop (several hours), and accurately weighed several times on an analytical balance. Appropriate blank flask/filter holder corrections were applied. Filtrable sediment values were obtained from the corrected net weight change of the filter holder with adherent gum values determined from the weight change of the test flask (4).

Reagents

The base fuel for the present study is DFM refined from Paraho crude shale oil by SOHIO. This fuel, produced in the U.S. Navy's Shale-II demonstration, is well-characterized (4). It was available with (sample "D-1") and without (sample "D-11") antioxidant added. The antioxidant, 2,4-dimethyl-6-*t*-butylphenol (AO-30), was present at the 24 mg/l level in fuel D-11. No other additives were present in either sample. All nitrogen compounds used as dopants were pure by NMR, capillary GC, and/or mp. Fresh DMP was stored frozen under nitrogen so as to prevent autoxidation and it remained colorless under this storage. The concentration matrix was prepared by appropriate dilution of a quantity of stock-doped fuel solution (typically 450 ppm w/v nitrogen).

RESULTS AND DISCUSSION

Accelerated fuel stability tests are important to the producers of fuels and to those performing research on chemical instability phenomena (5). The majority of these tests measure sediment weight in order to estimate fuel instability, and test temperatures have varied between ambient and

150°C. Although higher temperatures enable storage tests to be completed in minimum time periods, the accompanying uncertainty of the significance of the observed conditions may be dominant. Figure 1 summarizes a time-temperature matrix for several accelerated fuel stability tests which have appeared in the literature. It is noteworthy that a majority of the stability tests depicted fall close to the solid line, which represents a doubling of test time for each 10°C drop in temperature. The line extrapolates to approximately one year of ambient storage. The present study has concentrated on the lower temperature range (43, 65, and 80°C) in an effort to examine the reliability of using such accelerated storage tests as measures of ambient stability. As indicated by Figure 1, stress times were selected to bracket the solid line at each of the three temperatures.

The promotion of sediment formation in fuels by DMP has been reported to be a facile process, characterized by an activation energy of 10-15 kcal/mol (1,2). When subjected to storage at 43°C for periods of time ranging from 52 to 179 days DMP-doped Shale-II DFM formed large amounts of insoluble material. The DMP was added to samples D-1 and D-11 at concentrations of 0, 45, 135, 270 and 450 ppm N (w/v), and vented trials were also conducted at 45 and 450 ppm. The deviation between duplicate stress samples was small and indicated very good reproducibility for the test procedure. In general, the adherent gum comprised only 5-10% of the total insolubles. Venting of test flasks did not affect the amount of insoluble material formed. In a similar manner, the presence of the antioxidant (AO-30) in D-11 was of no consequence.

The DMP test matrix at 80°C (stress lengths 4-28 days) provided results which compared exceptionally well with those obtained at 43°C. In general, results at 65°C (11-50 days) also showed good agreement with the other two temperature regimens, although agreement between duplicates was somewhat less satisfactory at this temperature. The results for 80°C stresses of DMP-doped D-1 are shown in Figure 2. The first-order type of behavior which was observed with DMP is illustrated in Figure 3. At all temperatures examined, the amount of total insoluble material formed was directly proportional to the initial concentration of DMP. Furthermore, nitrogen balance calculations are able to account for all of the DMP (after stress) as either unreacted or incorporated into the sediment produced. Nitrogen-specific capillary GC (Hall detector) did not detect any nitrogenous intermediates in the liquid phase.

The sediments produced in all instances have been found to be rich in nitrogen (ca. 12% by weight), and an empirical formula of $C_6, 3H_6, 7NO_{1.4}$ has been determined (oxygen by direct analysis). The energy of activation for the production of total insolubles was calculated to be 11.7 and 11.6 kcal/mol for fuels D-1 and D-11, respectively. No induction periods were observed.

Filtrate hydroperoxide levels were determined in stressed samples by iodometric titration (ASTM D-1583-60). DMP-doped DFM samples exhibited very low peroxide numbers after stress. The DMP either prevents hydroperoxides from forming, or else reacts with any hydroperoxides which have formed. Results obtained in benzene indicated that formation of hydroperoxides from solvent molecules is not a prerequisite for DMP-promoted sedimentation. Mechanistic studies are continuing. Figure 4 shows the peroxide numbers obtained for D-1 and D-11 fuel blanks (un-doped) after 80°C stress. The antioxidant present in D-11 was seen to protect the fuel out to about 21 days, at which point the peroxide numbers increased sharply. Fuel D-11 contained no detectable hydroperoxide prior to stress.

A survey of other nitrogen compounds as fuel dopants has been undertaken in D-1 fuel. The results of 80°C - 14 day trials (unvented) with 450 ppm N (w/v) of a variety of compound classes are shown in Table I. Alkyl substituted pyrroles were found to be the most active species, with pyridines and quinolines less active. Peroxide numbers were low in the case of most pyrrole trials, and the sediments obtained were rich in nitrogen. Curiously, Knorr's pyrrole (2,4-dimethyl-3,5-dicarbethoxy-) was a most inactive species. Thus, electronic factors may be important for pyrroles.

CONCLUSIONS

A common reaction pathway appears to exist for DMP-promoted sedimentation in DFM. Results obtained are consistent with those of other workers (2). A high-precision gravimetric method of fuel storage stability determination has been developed.

ACKNOWLEDGMENT

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FIGURE 1
Time-Temperature Correlation for
Accelerated Fuel Stability Tests

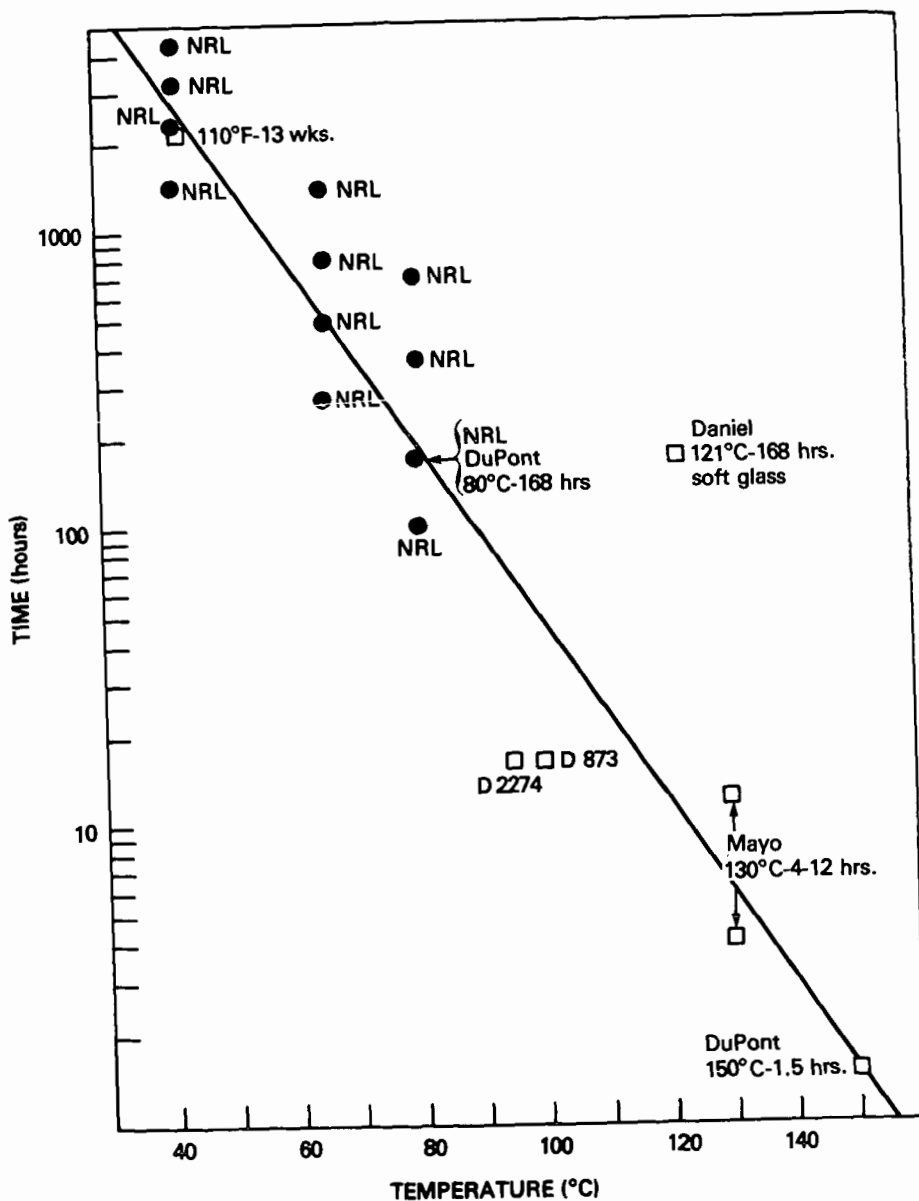


FIGURE 2
Total Deposits for Shale-II DFM
(D-1) with DMP Added - 80°C

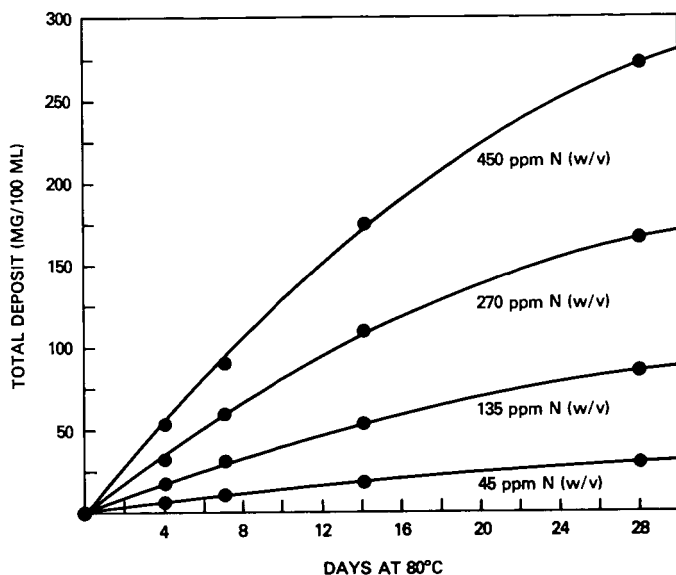


FIGURE 3
Total Deposit as a Function of Initial DMP
Concentration Added to DFM (D-11)
28 Day Stress at 80°C

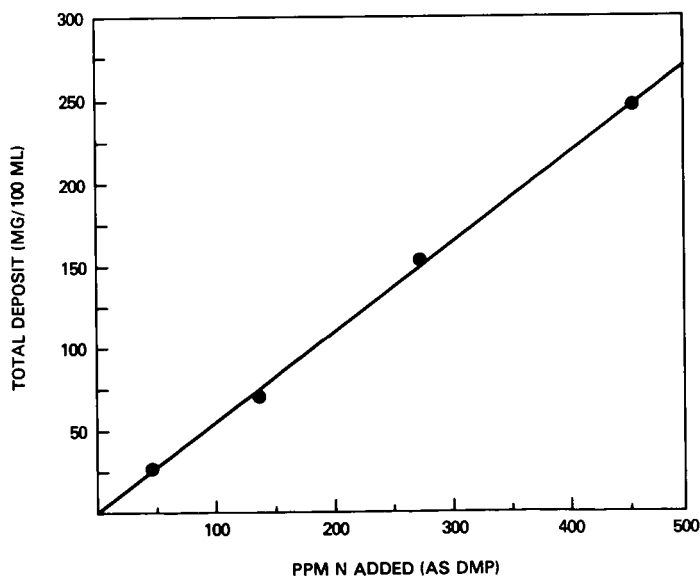


FIGURE 4
Peroxide Numbers for DFM
(D-1 and D-11) at 80°C

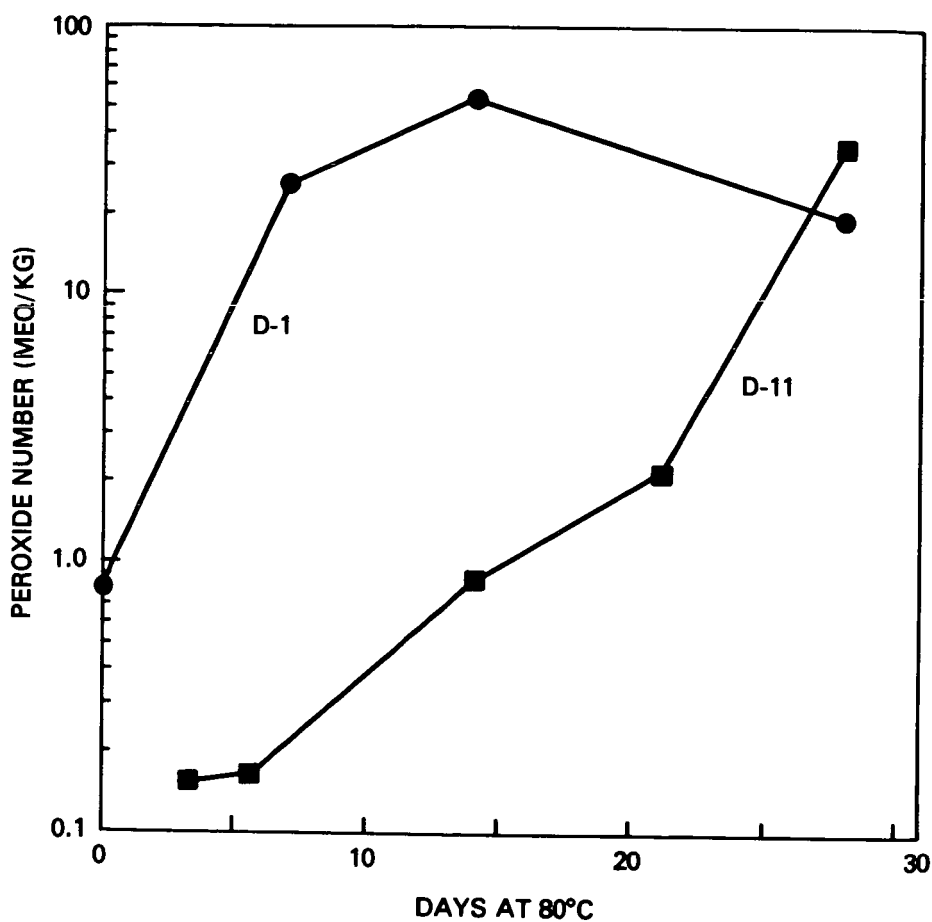


TABLE I
RELATIONSHIP OF NITROGEN COMPOUND STRUCTURE
TO SEDIMENTATION IN DFM (D-1)
(Listed in Approximate Order of Activity)*

<u>Group A (>100 mg/100 ml)</u>	<u>Group C (3-10 mg/100 ml)</u>	<u>Group D (<3 mg/100 ml)</u>
2,3,4,5-Tetramethylpyrrole	2,3-Dimethylindoline	3,5-Dimethylpyridine
Dodecahydrocarbazole	2,6-Dimethylpyridine	3,5-Dimethylpyrazole
2,4-Dimethylpyrrole	2-Methylpyrrole	4-Methylquinoline
2,3-Dimethylpyrrole	4-T-Butylpyridine	2-Methylquinoline
1,2,5-Trimethylpyrrole	3-Methylisoquinoline	3-Methylpiperidine
	Pyrrole-2-Carboxaldehyde	2-Methylpyrazine
	1-Methylpyrrolidine	2,5-Dimethylpyrazine
<u>Group B (10-100 mg/100 ml)</u>	2,6-Dimethylquinoline	Indole-3-Carboxaldehyde
Pentamethylpyrrole	2-Benzylpyridine	5,6,7,8-Tetrahydroquinoline
3-Methylindole	4-Iso-Butylquinoline	5-Ethyl-2-Methylpyridine
	2-Methylpiperidine	Trans-2,5-Dimethylpiperazine
	Pyrrolidine	2-Methylindole
	2-Acetyl-1-Methylpyrrole	2-Methylpyridine
		1,2,3,4-Tetrahydroquinoline
		2,6-Dimethylpiperidine
		2,4-Dimethyl-3,5-Dicarbethoxypyrrole

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- (2) Frankenfeld, J. W., Taylor, W. F., and Brinkman, D. W., "Fundamental Synthetic Fuel Stability Study", EXXON R and E Co., Rpt. No. DOE/BC/10045-23, March 1982.
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